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Biorelease Multinutrient Fertilizers for High-altitude Agriculture

Field Trials in the Kumaon and Garhwal Himalayas, India

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*We studied the effect of new types of slow-release micronutrient fertilizers on crop production in the Himalaya. These were biorelease fertilizers of zinc, iron, manganese, copper, boron, and molybdenum synthesized in a laboratory. Trials were conducted at Pithoragarh (1240 m), Kumaon Himalaya, with radish (*Raphanus sativus*) followed by amaranthus (residual effect;* Amaranthus blitum*), and at Auli (2900 m), Garhwal Himalaya, with cabbage (*Brassica oleracea *L. var.* capitata*) and thereafter lahi (residual effect;* Brassica rugosa*). Increases in yields of radish of 61% and increases in its vitamin C content by 105% were observed with low dosages of micronutrients. The yield of cabbage also increased by 98%, and its vitamin C content increased by 46%. In the residual effect trial, lahi (a leafy vegetable) produced a remarkable 164% increase in yield that was statistically significant at a 1% level. Overall, the data suggest that biorelease fertilizers are very effective at low dosages. They would be particularly suitable for crop production in mountainous regions.*

Keywords: *Biorelease; fertilizers; field trials; vegetables; multinutrients; altitude; Himalaya; India.*

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Introduction

Farming in the Himalaya is a painstaking task. Except in the valleys, mechanized farming is not possible. Farms adjacent to rivers are sometimes on relatively flat ground, but they are often subjected to floods. By and large, creation and maintenance of farmland in this region are critical. Developing a scientifically testable farming system in such a highly varied environment is not easy. Soil characteristics may change considerably within a few meters, and it is generally difficult to prepare an adequate number of identical microplots for trials. Soluble fertilizers and pesticides need to be used with maximum caution because people collect potable water from the streams adjacent to farmlands. Finally, high rainfall, frequent landslides, and long, harsh winters compound these problems.

Notwithstanding the aforesaid constraints, efforts have been made to carry out fertilizer trials, but they have been largely restricted to macronutrients (Singh 1998; Sharma 2004). However, in an environment where soil properties are highly variable owing to differences in parent materials and other geological factors, the nature and content of micronutrients can vary dramatically (Sharma et al 2006; Sharma and Chaudhary 2007) and affect crop growth to a considerable extent. The few trials that have been conducted have only tested 1 or 2 soluble micronutrients (Katyal 1985; Deb 1990), and these findings are not applicable on a wider scale.

There is a need to conduct trials with a combined dose of essential micronutrients and apply the knowledge gained as a general principle. Because of the factor of variability, it is not possible to analyze all soils and make recommendations accordingly. It is also not desirable to apply soluble fertilizers for environmental reasons. A solution to this problem, however, is now available following the development of slow-release micronutrient fertilizers of the biorelease type (Ray et al 1993, 1997; Varadachari 1999; Bhattacharya et al 2007). In these materials, micronutrients are attached to a polyphosphate backbone. They are practically insoluble in water but almost completely available to plants as evidenced by their solubility in DTPA (diethylene triamine penta acetic acid) and citrate. They are called “biorelease” because the mechanism of nutrient release is through solubilization by root exudate acids. As expected, these compounds have considerable residual effect on succeeding crops (Varadachari 1992); this property is very important in a fragile ecosystem.

The study presented here was designed as follows: (1) biorelease fertilizers were prepared with some essential micronutrients, (2) 2 suitable mixtures of them were formulated, (3) trials were carried out in 2 widely different areas, followed by residual effect trials, (4)

TABLE 1 Analysis of biorelease fertilizers.

Biorelease micronutrients	Major chemical constituents (%)	Solubility (%)		
		Water	0.005 M DTPA	0.33 M citric acid
Zinc (Zn)	ZnO: 26.1, NH_4^+: 10.5, P_2O_5: 43.5	2.4	100	100
Copper (Cu)	CuO: 17.2, NH_4^+: 20.3, P_2O_5: 47.5	4.5	100	100
Iron-manganese (Fe-Mn)	Fe_2O_3: 5.4, MnO_2: 2.7, MgO: 18.4, P_2O_5: 34.5	0.2	90	95
Boron (B)	B_2O_3: 20.1, Na_2O: 12.6, MgO: 15.6, P_2O_5: 44.4	5.6	34.9	100
Molybdenum (Mo)	MoO_3: 4.5, Na_2O: 13.0, MgO: 12.9, P_2O_5: 45.6	6.6	100	100

analyses were conducted of yield increase and vitamin C, a constituent especially critical to human health at high altitudes, and finally (5) a general conclusion was drawn.

Material and methods

Synthesis of biorelease fertilizers

Five types of biorelease fertilizers were synthesized in a laboratory.

1) Zinc fertilizer: The biorelease Zn fertilizer was prepared by reacting zinc ash and phosphoric acid (molar ratio Zn:P = 1:2) in a muffle furnace at 300°C until polyphosphate of an optimum chain length was produced (Ray et al 1990, 1993). It was neutralized with ammonia, then dried, ground, and sieved through a 100-mesh British Standard (BS) sieve.

Fertilizer was analyzed for the major chemical constituents (viz Zn, N, and P). This was done by dissolving a sample in 1 N HCl, followed by determination of Zn by atomic absorption spectroscopy (AAS) and N using the Kjeldahl method (Jackson 1973). For the analysis of P, a sample was fused in NaOH, and P was determined by spectrophotometry as the reduced molybdophosphate (Jackson 1973). Solubility of the fertilizer in water, 0.33 M citric acid (Ray et al 1993), and 0.005 M DTPA (Lindsay and Norvell 1978) was also determined.

2) Copper fertilizer: Copper carbonate and phosphoric acid (Cu:P = 1:3 molar ratio) were reacted at 300°C to produce linear copper polyphosphate of the desired chain length (Ray et al 1991a, 1997). The product was neutralized with ammonia, then dried, ground, and sieved through a 100-mesh BS sieve. The sample was dissolved in 1 N HCl and analyzed for Cu by AAS and for N and P as stated for zinc fertilizer. Solubility of the fertilizer was also assessed as before.

3) Iron-manganese fertilizer: A polyphosphate-based compound, containing both iron and manganese in biorelease forms, was prepared (Varadachari 2004a) by reacting goethite, pyrolusite, magnesia, and phosphoric acid (Fe:Mn:Mg:P = 2:1:1:8.2). Polymerization reaction was done at 200°C. The product of the appropriate degree of polymerization was neutralized with MgO, dried, powdered, and sieved through a 100-mesh BS sieve. The fertilizer was dissolved in 1 N HNO_3 and analyzed for Fe (ophenanthroline complex) and Mn (permanganate) by spectrophotometric methods (Jeffery et al 1991); Mg was analyzed by AAS, and P and solubility were analyzed as described for zinc fertilizer.

4) Boron fertilizer: Boric acid, sodium carbonate, magnesia, and phosphoric acid were reacted at 300°C to produce a long-chain metaphosphate (Ray et al 1991b). This was ground and sieved through a 100-mesh sieve. After dissolving in 1 N HCl, the solution was analyzed for B, Na, and Mg by AAS. Analysis of P and solubility were done as described for zinc fertilizer.

5) Molybdenum fertilizer: Molybdenum trioxide, sodium carbonate, magnesia, and phosphoric acid were heated at 300°C until the metaphosphate was formed (Varadachari 2004b). This polymolybdophosphate was ground and sieved (100 mesh). After dissolving in 1 N HCl, Mo was analyzed by the thiocyanate method (Jeffery et al 1991), Na was analyzed by flame photometry, and Mg and P were analyzed as described for zinc fertilizer.

Constituents of all biorelease fertilizers are presented in Table 1. Suitable mixtures of these fertilizers were applied.

Soil information

Field trials were conducted at the Defence Agricultural Research Laboratory (DARL) farms in Uttaranchal, India, specifically at Auli (31°N; 79°E; 2900 m; rainfall 1200 mm), Garhwal Himalaya, and Pithoragarh (29°N; 80°E; 1240 m; rainfall 1500 mm), Kumaon Himalaya (Figure 1). Auli is located on a steep slope and is a popular ski resort in winter. Pithoragarh is a broad valley.

Soil samples (Ap horizon, 0–15 cm) collected from both locations were air dried and passed through a 2-mm-

FIGURE 1 Location of study areas in India. (Map by Christian Hergarten; background: Google Earth)

mesh sieve. Soils were analyzed for pH (Thomas 1996), conductance (Rhoades 1996), and organic carbon by dichromate oxidation (Nelson and Sommers 1996); this value was converted to organic matter by multiplying by the factor 1.724 (Jackson 1973). Available Zn, Cu, Fe, and Mn were extracted with 0.005 M DTPA and determined by AAS (Lindsay and Norvell 1978); exchangeable Ca and Mg were extracted with 1 N ammonium acetate (Jackson 1973) and analyzed by AAS (Perkin Elmer 2380). Available Mo was extracted with acid ammonium oxalate (Sims 1996) and determined spectrophotometrically (AIMIL, spectrochem MKII) as described previously. The results of soil analysis are described later.

Auli soil is loose textured, well drained, and acidic (coarse loamy, mixed, thermic, humic Dystudept, with sandy loam texture, pH 4.9, conductance 1.11 dS m^{-1}, organic matter 37.9 g kg^{-1}). Relatively high organic matter levels were found because this area was a recent forest clearing. Pithoragarh soil is light textured, stony, near neutral in reaction, and low in organic matter (loamy, skeletal, mixed, thermic, typic Endoaquent, texture loam, pH 6.3, conductance 1.70 dS m^{-1}, organic matter 20.5 g kg^{-1}). The nutrient contents (in mg kg^{-1}) of the soils from Auli and Pithoragarh were respectively, N 1900, 1030; P 115, 43; Ca 1408, 1584; Mg 103, 290; Zn 5.0, 3.5; Cu 1.4, 3.8; and Fe 68, 115. The data do not reveal any deficiency of micronutrients. However, critical limits of micronutrients are different for different soils as well as for crops; therefore, only crop experiments can reveal the true status of micronutrients in soils (Mortvedt et al 1972; Biswas and Tewatia 1988; Fageria et al 2002).

Field trials

Primary effects of the fertilizers, as well as their residual effects, were studied on vegetables at both the aforementioned locations. Experiments were conducted in randomized block design (RBD) with a control and 3 different doses of biorelease formulations. For the first crop at Auli, there were 4 treatments with 6 replicates (plot size 6 m^2; see Table 2). Control plots were not treated with any of these nutrients. All treatments contained equal levels of N, P, and K at 100:70:70 kg/ha. Mg additions were also equalized on all plots. For the second crop of amaranthus, no further biorelease fertilizers were applied; only N, P, and K fertilizers were added, as above.

At Pithoragarh, there were 6 treatments with 6 replicates in each case (plot size 6.5 m^2; see Table 3). Quantities of the nutrients as well as the ratios were varied for each treatment. All treatments contained an equal level of N, P, and K at 100:70:70 kg/ha. Additions of Mg and S were also equalized on all plots. For the second crop of *lahi*, no further biorelease fertilizers were used; only N, P, and K fertilizers were added, as above.

There were fewer treatments and doses at Auli because of limitations in the availability of suitable land at one spot. The number of replicates, however, could not be

TABLE 2 Fertilizer treatments at Auli; first crop: radish; second crop: amaranthus (plot size: 6 m^2). V_1–V_3 are biorelease fertilizers. All treatments contain an equal level of N, P, and K at 100:70:70 kg/ha. For the second crop (amaranthus), no further biorelease fertilizers were used; only N, P, and K fertilizers were added.

Treatment	Nutrients added (kg/ha)					
	Zinc (Zn)	Copper (Cu)	Iron (Fe)	Manganese (Mn)	Boron (B)	Zn:Cu:Fe:Mn:B
Control	0	0	0	0	0	–
V_1	1.20	0.60	0.90	0.45	1.20	1.000:0.500:0.750:0.375:1.000
V_2	1.80	0.90	1.20	0.60	2.25	1.000:0.500:0.670:0.330:1.250
V_3	2.40	1.20	1.80	0.90	3.00	1.000:0.500:0.750:0.375:1.250

TABLE 3 Fertilizer treatments at Pithoragarh; first crop: cabbage; second crop: *lahi* (plot size: 6.5 m^2). R_1–R_5 are biorelease fertilizer treatments. All treatments contain equal levels of N, P, and K at 100:70:70 kg/ha. For the second crop of *lahi*, no further biorelease fertilizers were used; only N, P, and K fertilizers were added.

Treatment	Nutrients added (kg/ha)						
	Zinc (Zn)	Copper (Cu)	Iron (Fe)	Manganese (Mn)	Boron (B)	Molybdenum (Mo)	Weight ratios: Zn:Cu:Fe:Mn:B:Mo
Control	0	0	0	0	0	0	–
R_1	1.20	0.36	1.50	0.75	1.20	0.01	1.000:0.300:1.250: 0.625:1.000:0.008
R_2	2.40	0.36	1.50	0.75	1.20	0.01	2.000:0.300:1.250: 0.625:1.000:0.008
R_3	2.40	0.36	1.50	0.75	2.40	0.01	2.000:0.300:1.250: 0.625:2.000:0.008
R_4	2.40	0.72	1.50	0.75	1.20	0.01	2.000:0.600:1.250: 0.625:1.000:0.008
R_5	2.40	0.72	1.50	0.75	2.40	0.02	2.000:0.600:1.250: 0.625:2.000:0.016
X	2.40	0.72	1.50	0.75	2.40	0.02	2.000:0.600:1.250: 0.625:2.000:0.016

reduced because the terrains there are not uniform over a fairly wide area. Additionally, at Pithoragarh, where suitable land was available, a treatment with one particular dose of soluble micronutrient salts was carried out for comparison.

All treatments were equalized for N, P, and SO_4^{2-} additions. Thus, to compensate for the P in the biorelease fertilizers, the amount of DAP (diammonium phosphate) added to these plots was reduced so that the total P added was the same on all plots. Differences in the additions of DAP to the plots would lead to differences in amounts of N added. Therefore, N addition was equalized by adding calculated amounts of urea in each plot. Thus, in plots treated with smaller amounts of DAP, larger amounts of urea were added such that N fertilization was the same on all plots. Amounts of sulfate were equalized by addition of K_2SO_4. Since this also provides K, further additions of KCl were made so as to maintain uniform K levels on all plots. For the residual effect studies, no micronutrient fertilizers were added. Only NPK fertilization was done, maintaining uniform application on all plots.

TABLE 4 Field trials at Auli. Note: There were 6 replicates for each treatment. V_1–V_3: biorelease fertilizers; V_1 was the optimal biorelease fertilizer treatment.

Treatment	Radish		Amaranthus (residual effect)
	Yield (kg/ha)	Vitamin C (mg/100g)	Yield (kg/ha)
Control	5360	6.5	822
V_1	8650[b)]	13.5[c)]	1405
V_2	8080[a)]	9.2	950
V_3	9320[b)]	12.2[c)]	1056
$CD_{0.1}$	2483	–	–
$CD_{0.05}$	3067	3.3	–
$CD_{0.01}$	–	4.7	–

[a)] Significant at 10% level.
[b)] Significant at 5% level.
[c)] Significant at 1% level.

TABLE 5 Field trials at Pithoragarh. Note: There were 6 replicates for each treatment. CD values are given only where the *F* test shows significance. R_1–R_5: biorelease fertilizers; X: water soluble fertilizers.

Treatment	Cabbage				*Lahi* (residual effect)	
	Yield (kg/ha)		Diameter of head (cm)	Vitamin C (mg/100 g)	Yield (kg/ha)	Vitamin C (mg/100 g)
	Total weight	Weight of edible part				
Control	35,837	15,023	36.2	23.6	4670	42.1
R_1	41,137	21,628	44.1[c)]	33.6[c)]	12,350[c)]	71.9[c)]
R_2	50,891[a)]	24,347[b)]	45.0[c)]	32.2[c)]	10,384[b)]	63.4[c)]
R_3	53,886[b)]	23,426[b)]	45.3[c)]	32.9[c)]	10,906[c)]	78.0[c)]
R_4	51,306[a)]	20,277	41.9[b)]	31.6[c)]	9032[b)]	78.5[c)]
R_5	57,988[b)]	29,693[c)]	44.7[b)]	34.5[c)]	7896	64.1[c)]
X	56,529[b)]	18,633	42.5[b)]	27.8[c)]	9094[b)]	62.7[c)]
$CD_{0.1}$	13,386	6744	–	–	–	–
$CD_{0.05}$	16,221	8172	5.5	3.2	4316	–
$CD_{0.01}$	–	11,198	7.6	4.0	5853	8.4

[a)] Significant at 10% level.
[b)] Significant at 5% level.
[c)] Significant at 1% level.

At Auli, the first crop was radish, and the succeeding crop was amaranthus. At Pithoragarh, the crops were cabbage and *lahi*, respectively. After harvesting, the yield from each microplot was recorded. With cabbage, head diameter was also noted.

Statistical analysis

Data were statistically analyzed by 1-way analysis of variance (ANOVA) and F-test of the significance of the differences at 5% and 1% levels, followed by determination of the least significant difference (LSD) at 5% and 1% probability levels (Gomez and Gomez 1984). Results are shown in Tables 4 and 5.

Analysis of plant samples

The vegetable samples were washed, chopped, dried at 60°C, and digested with tri-acid mixture ($HClO_4$:HNO_3:H_2SO_4 = 4:10:1, v:v:v) for analysis of Zn, Fe, and P by the methods described already.

Fresh samples (prior to drying) were also analyzed for their vitamin C content by extracting with oxalic acid and titrating with 2,6-dichlorophenol-indophenol (Davies et al 1991).

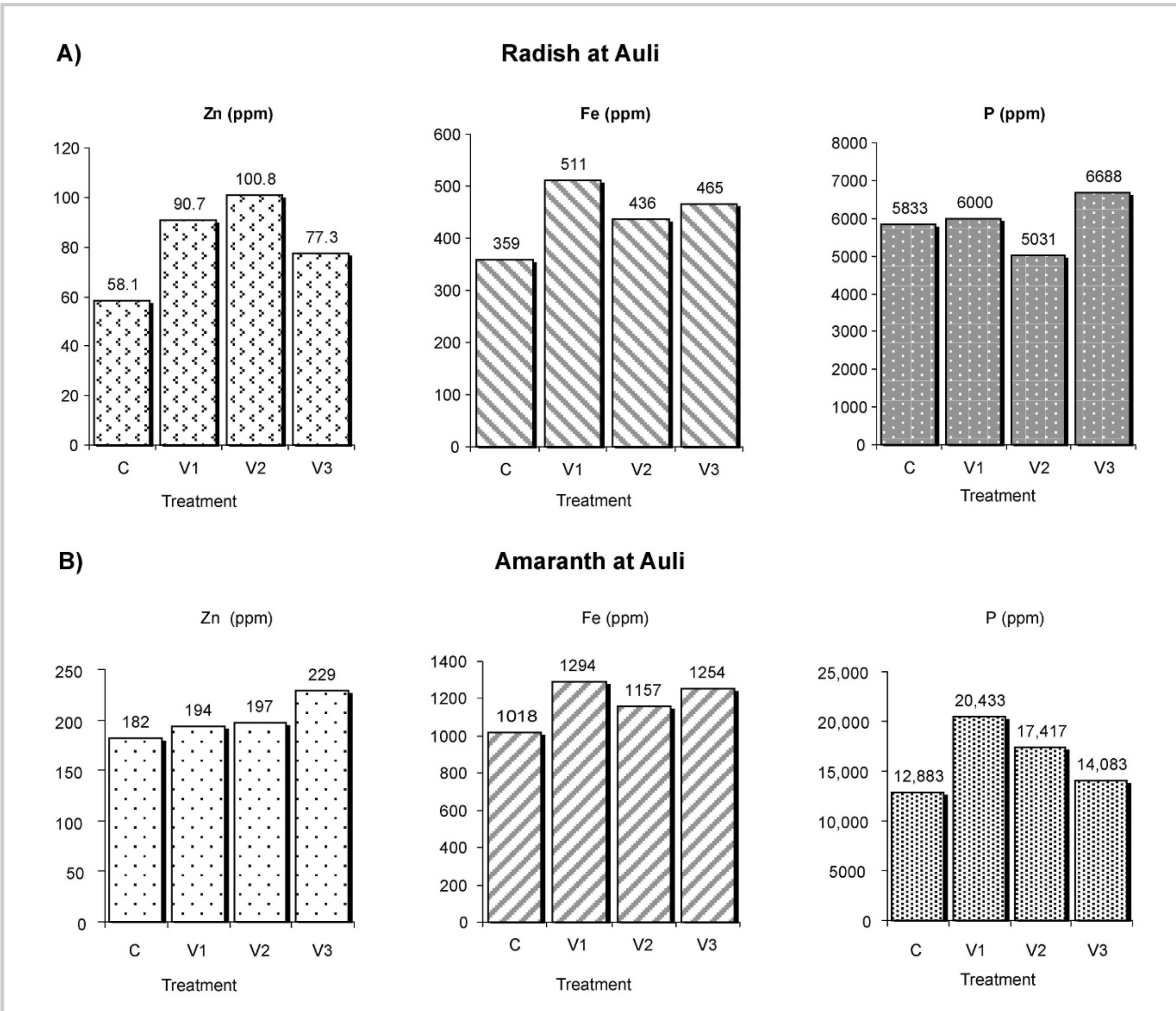
Results and discussion

Analytical data and solubility characteristics of the fertilizers are shown in Table 1. It may be noted that whereas the water solubility of all these fertilizers is very low, solubility in organic chelates is very high. Nutrient ions soluble in DTPA or citrate are considered to be available for plant uptake (Lindsay and Norvell 1978). Therefore, the nutrient ions in these fertilizers, although water-insoluble, are in a plant-available form. In the soil, secretion of various organic acids by plant roots (Epstein 1972) would cause solubilization of the ions and subsequent uptake by the plant. The biorelease fertilizers, therefore, function as a storehouse of nutrients from which plants can take up according to need. Unlike in water-soluble fertilizers, here the nutrients are available throughout the growth period and are, consequently, highly efficient, as demonstrated in numerous experiments (Varadachari 1992; Saikh et al 2007).

Radish (*Raphanus sativus*): Auli

Experimental data in field trials with radish at Auli are shown in Table 4 and Figure 2. A large increase in yield of radish was observed on the biorelease-fertilizer-treated plots. The increase was 61% for treatment V_1 and 74% for treatment V_3; these values are statistically significant at the 5% level compared to the control treatments. The fertilizer appeared to be effective even at very low doses of micronutrients. For treatment V_1 (in which Zn application was 1.2 kg/ha), Zn uptake increased significantly, by 56% (Figure 2), and content of Fe

FIGURE 2 Nutrient levels (ppm of dry weight) in radish and amaranthus grown in Auli. With radish: LSD 0.05% for Zn (31.4), Fe (96.4), P (441). With amaranthus: LSD 0.05% for Zn (24), Fe (220), P (4288).

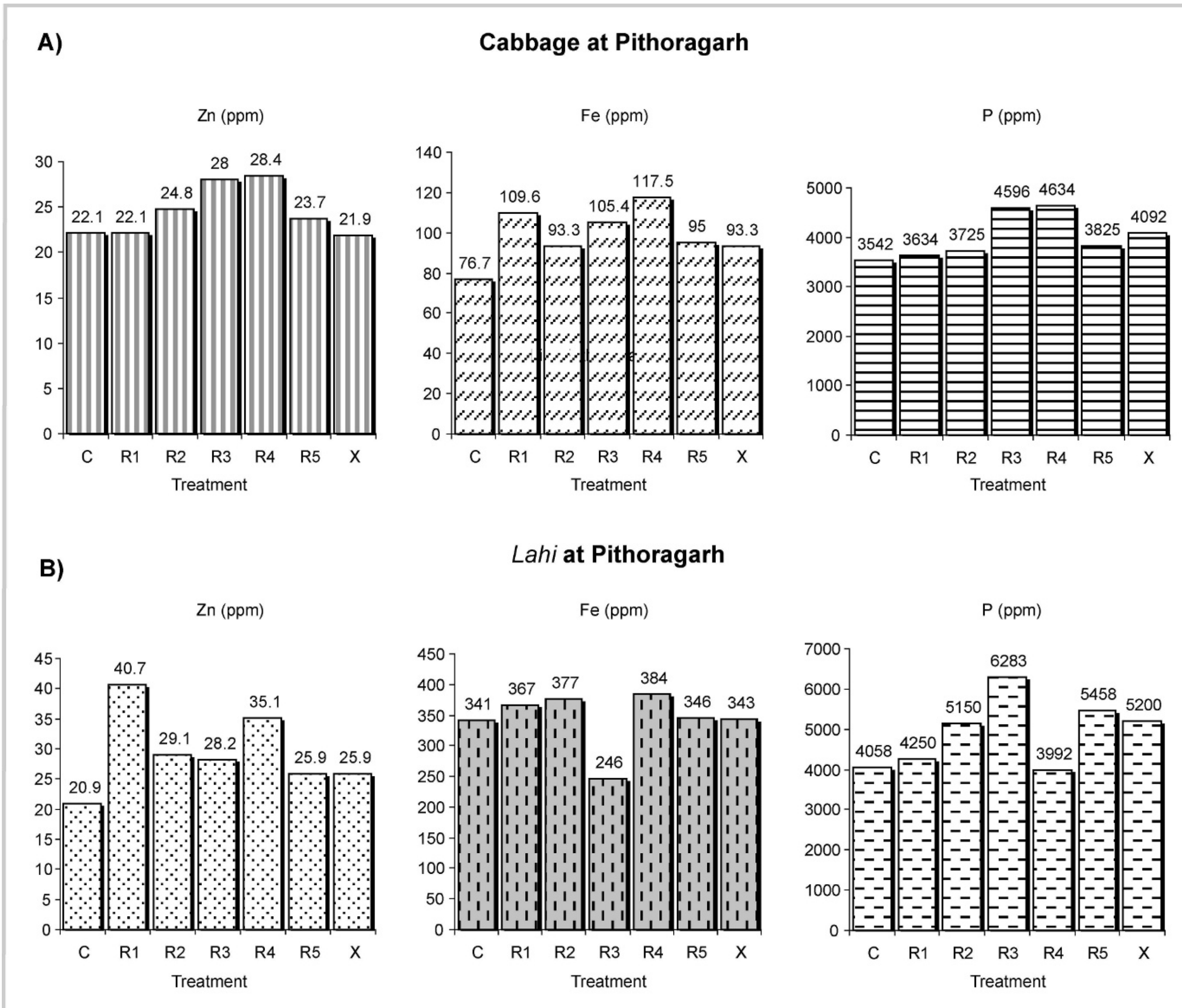


increased significantly, by 42% over the control treatment, although the soil contained both these ions in sufficient quantities. This implies that Fe in the biorelease fertilizers was more effective than Fe in the soil. Treatment V_1 showed significant uptake of Fe over control at 1% level. P content of the radish increased by about 167 ppm in V_1 and 855 ppm in V_3 (significant). A remarkable increase in vitamin C content was observed with treatment V_1, showing an increase of 108% over control at 1% level. Vitamin C content in treatment V_3 was also significant at 1% level over control. It should also be mentioned that the radish from plots treated with the biorelease fertilizers had a better flavor and stronger taste than those from control plots.

Amaranthus (*Amaranthus blitum*): Auli

Amaranthus was planted as the crop for residual effect studies after the radish crop was harvested. On these plots, no further biorelease fertilizers were applied; only NPK application was done. Crop growth was poor due to low rainfall and nonavailability of irrigation ,and, therefore, statistical analysis of the data was not conclusive. However,

FIGURE 3 Nutrient levels (ppm of dry weight) in cabbage and *lahi* grown in Pithoragarh. With cabbage: LSD 0.05% for Zn (6.1), Fe (25.7), P (not significant). With *lahi:* LSD 0.05% for Zn (16.4), Fe (not significant), P (not significant).



there was an increase in yield of 71% at the lowest level of biorelease fertilizer application (Table 4).

It is noteworthy that the contents of all nutrients were remarkably high in the amaranthus plant (Figure 2). This suggests that amaranthus is a good source of mineral nutrition for humans. Zn content, even in control treatments, was as high as 182 ppm. On Zn application (V_3), this increased to 229 ppm (significant at 5%); Fe showed a 27% increase over control. Uptake of Fe was significant at 5% level in treatments V_1 and V_3. In V_1, P content increased by 59%. Higher levels of biorelease fertilizers (V_2 and V_3) did not significantly enhance the yields and nutrient levels over V_1.

Cabbage *(Brassica oleracea* L var. *capitata*): Pithoragarh

Yields of cabbage increased substantially after application of biorelease fertilizers (Table 5). Treatment R_5 produced the highest yield increase of total weight of plant by 22,151 kg/ha (or 62%) over the control; this value is statistically significant. Treatment R_5, which appears to be the optimal, produced an edible yield increase of 98%. Treatment R_5 differed from R_4 in the higher levels of B and Mo application; the consequent increase in cabbage yields was 9416 kg/ha. Treatment X, which had the same level of nutrients as R_5, showed a small increase in yield of cabbage (edible weight) over control, which was even less than in R_1. This revealed that yields obtainable with biorelease fertilizers were not obtainable with conventional micronutrients, even when dosages were doubled. The diameter of the heads of cabbage also increased significantly upon treatment with biorelease fertilizers.

Nutrient levels in the cabbage showed an overall increase (Figure 3). Zn showed a maximum significant increase of 29% in R_4. As Zn application increased from R_1 to R_2, Zn levels in cabbage also increased. Contents of Fe increased significantly, by about 43%, 37%, and 53% in biorelease treatments R_1, R_3, and R_4, respectively. Contents of P in the samples were highest at R_3, but this increase is not significant. It is noteworthy that in treatment X, the cabbage had only slightly lower levels of all nutrients than the equivalent treatment R_5. However, yields with R_5 were much higher than with X. This suggests that slower nutrient release over longer periods was more beneficial than a one-time release, as with conventional micronutrients. Vitamin C contents in cabbage from plots treated with biorelease fertilizer showed a remarkable increase (Table 5). The greatest increase, 46%, was observed in R_5; other R treatments showed similar increases. All these values are significant at the 1% level. Treatment X (conventional micronutrients) showed a small increase, which was not, however, significant at this level. In all respects, therefore, the conventional fertilizers performed poorly compared to the biorelease fertilizers.

Lahi (*Brassica rugosa*): Pithoragarh

Lahi, a leafy vegetable, was the experimental crop for studying the residual effect of the fertilizers. Remarkably good residual effect of the fertilizers was observed in the yield data (Table 5). At the lowest dose, R_1, yield increased significantly, to 164%. This is a phenomenal response considering the small amount of nutrients added to the previous crop. Treatments R_1, R_2, R_3, and R_4 showed an increase in yield over the control, significant at 5% level. Apparently, the *lahi* crop required very low dosages of micronutrients to produce very large increases in yield. Yield also increased with soluble fertilizers (X), but this was not statistically significant, even at the 10% level. Contents of Fe and P did not show statistically significant increases.

Results showed that crop yields increased in both locations regardless of soil attributes. Both soils were fairly high in organic matter (though Auli soil had higher organic matter) and did not show deficiency with respect to any of the micronutrients. However, responses to the micronutrients were significant, suggesting that despite a variation in soil properties at the 2 locations, fertilization with biorelease micronutrients can enhance productivity.

Conclusion

This study suggests that agricultural productivity in high-altitude regions may be substantially improved by the use of the new environment-friendly, biorelease multinutrient fertilizers. These fertilizers contain water-insoluble but plant-available micronutrients (Zn, Cu, Fe, Mn, Mo, and B) in addition to Mg and P. This multinutrient mixture was observed to be very effective at dosages very much lower than normal. There was a significant increase in the yields of vegetables, and produce was also nutritionally richer and higher in vitamin C content.

These results are significant for agriculture in mountainous regions. By improving crop yields at low fertilizer dosages, the economy of such regions could be substantially improved. Improvement in the nutritional quality of crops, in terms of micronutrients and vitamin C, has important health and social implications, particularly in the developing countries along the Himalayan range. Apart from use in regular agricultural lands, other mountain terrains that are too infertile could benefit from these fertilizers.

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